Landau Theory of the Reentrant Nematic-Smectic A Phase Transition

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Landau theory of the reentrant nematic-smectic A phase transition

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Résumé. — Nous montrons que le diagramme de phase *rentrant* de la transition nématique-smectique A, découle naturellement de la théorie de Landau si l'on admet qu'il existe une densité optimale pour l'obtention de l'ordre smectique. La forme de la ligne de coexistence dans le plan *P-T*, est correctement prédite par la théorie. Nous décrivons aussi le comportement *rentrant* des mélanges.

Abstract. — The reentrant, nematic to smectic A phase transition is shown to follow from the Landau theory if one assumes the existence of an optimum density for smectic ordering. The shape of the coexistence line in the *P-T* plane is fit exactly by this theory. The effects of concentration on reentrant behaviour are also explained.

Cladis and coworkers have recently demonstrated that for some liquid crystals, the boundary between nematic and smectic A phases in the *P*, *T* plane is *reentrant* in that at high enough pressures the nematic phase exists for temperatures both lower and higher than for the smectic phase [1]. In some materials that have a smectic-A to nematic phase transition which is not reentrant, reentrant behaviour can be induced by mixing it with a second liquid crystal that only has a nematic phase [2]. Cladis also observed that reentrant behaviour appears only in materials for which the smectic phase is of the bilayer type and suggested that at densities above some optimum value the interactions stabilizing smectic order would be suppressed by steric effects. The purpose of this article is to demonstrate that if one assumes the existence of this optimum density most of the observed properties of the reentrant transition are predicted by the Landau theory of the nematic to smectic A phase transition [3, 4].

Reentrant behaviour has also been observed at the normal to superconducting phase boundary in materials containing magnetic impurities [5] and in one of the ^{3}He phase transitions [6]. In view of the often used analogy between smectics and superfluids [3, 4] it is important to note that reentrant behaviour is simply a consequence of two competing interactions whose sum can be optimized through control of another variable. Its appearance in superconductors, ^{3}He and liquid crystals does not *necessarily* imply the microscopic interactions responsible for the effects, are analogous.

In the usual form of the Landau theory the difference between the free energy per unit mass of the smectic and nematic phases is expanded as a power series in the smectic order parameter $|\psi|$

$$F_s - F_N = f = \tfrac{1}{2} A |\psi|^2 + \tfrac{1}{4} B |\psi|^4 + \tfrac{1}{6} C |\psi|^6 \quad (1)$$

where $A \equiv a(T - T^*)$. If $B > 0$ the transition is second order and occurs at $T = T^*$; if $B < 0$ a first order transition occurs at $T = T^* + 3B^2/16\,aC$.

The Landau theory has been widely applied to a number of different phase transitions and examples where the order parameter couples to some other variable are also common [4, 7]. In the present case we want to describe coupling of $|\psi|$ to both the density ρ and the relative concentration x of a binary mixture. The simplest assumption is to add a term to eq. (1) of the form $g(\rho, x)\,|\psi|^2$, expand g as a power series in $(\rho - \rho_0, x - x_0)$ and keep only the leading terms. If we consider only the density term first, and choose ρ_0 to be the *optimum density* referred to above, the T^* appearing in eq. (1) can be replaced by

$$T^*(x, \rho) = T_0(x) + t_2(\rho - \rho_0)^2 \quad (2)$$

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where $t_2 < 0$ insures that $\rho \neq \rho_0$ suppresses the phase transition.

The general procedure [8] for obtaining the nematic to smectic phase boundary is to first obtain expressions for the pressure $P = \rho^2(\partial F/\partial\rho)_{x,T}$, and the chemical potentials

$$\mu' = (\partial F/\partial x)_{\rho,T}$$

and

$$\mu = F - x(\partial F/\partial x)_{\rho,T} + \rho(\partial F/\partial\rho)_{x,T}$$

for the two components and for both phases. Setting μ, μ', and P for the smectic phase equal to those of the nematic phase defines the phase boundary. From the equality of P one obtains the difference $\rho^s - \rho^N$ between the smectic and nematic densities

$$\rho^s - \rho^N \simeq \frac{a}{2}\rho^2\left(\frac{\partial T^*}{\partial\rho}\right)_x |\psi|^2 \quad \frac{\partial}{\partial\rho}(P)_x \qquad (3)$$

where the derivatives are evaluated at $\rho = \rho^N$ and $x = x^N$. From the equality of μ' one obtains

$$x^s - x^N \simeq \frac{a}{2}\left(\frac{\partial T^*}{\partial x}\right)_\rho |\psi|^2 \quad \left(\frac{\partial\mu'}{\partial x}\right)_\rho \qquad (4)$$

and the condition that $\mu_s - \mu_N = 0$ is only slightly different from the usual condition that $F_s - F_N = 0$ at the transition. It has exactly the same form, however, $T^*(x, \rho)$ is replaced by $T^*(x^N, \rho^N)$ and B is changed by the addition of two negative terms

$$-\frac{a^2}{2}\left[\frac{(\partial T^*/\partial x)_\rho^2}{\left(\frac{\partial\mu'}{\partial x}\right)_\rho} + \frac{(\partial T^*/\partial\rho)_x^2}{\frac{\partial}{\partial\rho}\left(\frac{P}{\rho^2}\right)_x}\right]. \qquad (5)$$

The equation obtained by minimizing $\mu_s - \mu_N$ with respect to ψ for given ρ^N and x^N is identical to the equation and the result obtained by minimizing eq. (1) at fixed ρ^s and x^s if the equalities described by eqs. (3) and (4) are taken into account. If the terms described by eq. (5) are small in comparison with the original value of $|B|$ they can be neglected regardless of whether $B < 0$, implying a first order transition, or $B > 0$ implying one of second order. On the other hand, since coupling between $|\psi|^2$ and either ρ or x makes a negative contribution to B it also increases the tendency to first order behaviour. Also, since for dilute solutions $(\partial\mu/\partial x)^{-1} \propto x$ one can reasonably expect that the effect of adding a second component to a pure material that exhibits a second order s — N transition may be to induce a tricritical point at some finite x.

Neglecting the terms described by eq. (5) the transition temperature can be obtained from eqs. (1) and (2) by setting $T - T^*(x^N, \rho^N)$ equal to either zero for a second order transition or $3\,B^2/16\,aC$ if it is first order. Taking

$$(\rho^N - \rho_0)/\rho_0 = -\alpha_N(T - T_0) + \beta_N(P - P_0),$$

where α_N and β_N are respectively the thermal expansion and compressibility for the nematic phase. The phase boundary surface is predicted to have the form

$$T_3[T_1(x) - T] = (T_2 - T + [\beta_N/\alpha_N]\,P)^2 . \qquad (6)$$

In figure 1 we show the fit of eq. (6) to data reported by Cladis *et al.* for a sample of pure 4-cyano-4'-octyloxy biphenyl (8OCB) [1]. In terms of the parameters of eq. (6) the maximum temperature, is indicated in figure 1 by $T_{(II)} = T_1(x)$ where $x = 0$, the pressure for this temperature $P_{(II)} = (\alpha_N/\beta_N)(T_{II} - T_2)$, the temperature, for which the pressure is a maximum $T_I = T_{II} - T_3/4$ and $P_I = (\alpha_N/\beta_N)[T_{II} + T_3/4 - T_2]$. The parameters for this fit are

$$T_1 = 83\ ^\circ\text{C}, \quad T_2 = 46.2\ ^\circ\text{C}, \quad T_3 = 22\ ^\circ\text{C}$$

and

$$\beta_N/\alpha_N = 23\ \text{K/kbar}.$$

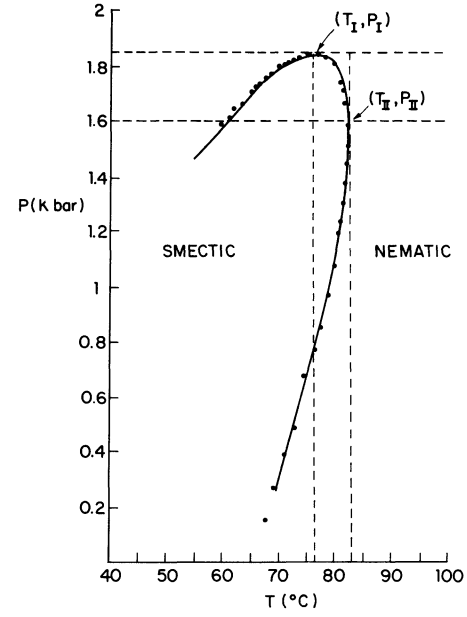

Fig. 1. — Typical reentrant nematic phase diagram. The dots are the experimentally determined points for 8OCB (see Ref. [1]). The solid line results from eq. (6) with $x = 0$ and parameters as specified in the text.

Although T_1, T_2 and T_3 are completely adjustable β_N/α_N can be estimated since the thermal expansion coefficient $\alpha_N \sim 10^{-3}\ \text{K}^{-1}$ for almost all condensed fluids and also for nematic liquid crystals [9, 10]. Also β_N can be obtained from sound speeds in either the isotropic or nematic phases [11]. Typical values for similar materials obtain $\beta_N^{-1} \sim 4$ or 5×10^{10} dyne.cm$^{-2} \simeq 40$ or 50 kbar obtaining very good agreement between the expected value of $\beta_N/\alpha_N \sim 20$ to 25 K/kbar, and the value that fits the data. This is the strongest evidence sup-

porting the premise that the phase boundary curvature can be interpreted in terms of an optimum density for smectic order.

Cladis already noted that in binary mixtures of N-p-cyanobenzylidene-p-nonylaniline (CBNA) and N-p-cyanobenzylidene-p-heptylaniline (CBHA) the maximum pressure P_I is a linear function of the ratio of CBNA to CBHA [12]. This follows from the above considerations if we take $T_0(x)$ to be a linear function of this ratio, e.g.,

$$T_0(x) = T_0 + t_1 y = T_0 + t_1[x/(1 - x)] \quad (7)$$

where

$$y = [\text{CBNA}]/[\text{CBHA}] = x/(1 - x) .$$

Since $T_1(x) - T_0(x)$ is a constant P_I is also linear in $x/(1 - x)$. Figure 2 contains one possible fit of eq. (6) to Cladis's data for this mixture using

$$T_1 = 42.85\ ^\circ\text{C}, \quad T_2 = 43.55\ ^\circ\text{C}, \quad T_3 = 25\ \text{K},$$
$$t_1 = 38.7\ \text{K} \quad \text{and} \quad \beta_N/\alpha_N = 19.4\ \text{K/kbar} .$$

Although the linear dependence of T^* on $x(1 - x)^{-1}$ is *ad hoc* it is interesting that it is sufficient to qualitatively describe all of the concentration effects. Furthermore, the ratio α_N/β_N is in reasonable agreement with the values expected from an optimum density model. More generally, one would certainly expect ρ_0 to depend on x and there is no reason why the other parameters shouldn't also. Although inclusion of these effects would undoubtably improve the fit it does not seem worthwhile without some specific microscopic model.

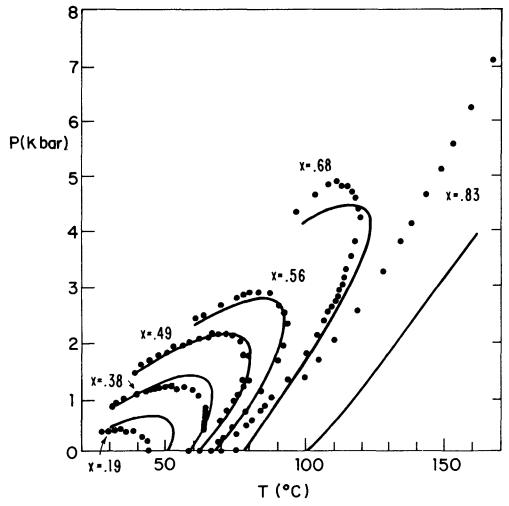

Fig. 2. — Fit of eq. (6) to the reentrant phase diagrams of binary mixtures of CBNA and CBHA, measured by Cladis *et al.* The concentration x = weight CBNA/weight [CBHA + CBNA] and the parameters are $T_1 = 42.85\ ^\circ\text{C}$, $T_2 = 43.55\ ^\circ\text{C}$, $T_3 = 25\ ^\circ\text{C}$, $t_1 = 38.7\ ^\circ\text{C}$ and $\alpha_N/\beta_N = 0.051\,6$ kbar/°C. The dots and solid lines have the same meaning as for figure 1.

If we take $P = 0$ in eq. (6) (i.e., atmospheric pressure) the nematic-smectic A phase boundary is predicted to have the same form, e.g.,

$$y - y_{Ns} + \beta(T_{Ns} - T)^2 = 0$$

that Cladis [2] used to describe her observations on binary mixtures of p[p-hexyloxy-benzylidene]-amino-benzonitrile (HBAB) and N-p-cyanobenzylidene-p-n-octyloxyaniline (CBOOA). Expressions for T_{Ns} and y_{Ns} in terms of the parameters in eq. (6) are easily obtained. Mixtures of 4-cyano-4′-hexyloxybiphenyl (6OCB) and (8OCB) behave similarly [12].

According to the Landau theory there is no essential difference between the high and low temperature nematic phases and experiments support this. For example Cladis's measurements of the bend elastic constant K_3 in HBAB-CBOOA mixtures behaved similarly on both sides of the smectic phase. Furthermore at concentrations high enough that a smectic phase does not appear (i.e., $x > x_0$) the standard Landau theory [3] predicts that both the bend and twist elastic constants, K_3 and K_2 should diverge as the correlation length. For $x > x_0$ this will have the form $[(T_{Ns} - T)^2 + (\Delta T)^2]^{-1/2}$. Figure 3 demonstrates the fit between this expression and Cladis's data [2]. Schaetzing *et al.* [13] have done light scattering studies on the nematic phase of 6OCB-8OCB mixtures as the smectic is approached from both higher and lower temperatures. Although for $x < x_0$ the tran-

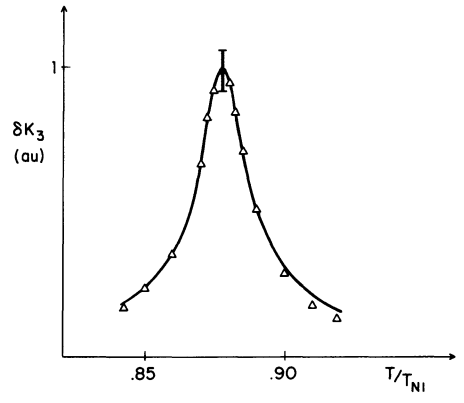

Fig. 3. — Enhancement of the bend elastic constant K_3 as a function of temperature, in a mixture of 12.67 % by weight of HBAB in CBOOA, as a function of the reduced temperature $t = T/T_{N1}$. The triangles are estimated from the figure 3 of reference [2] by subtracting to the critical field H_c ($\propto K_3$) at the reduced temperature T/T_{N1}, the background value H_c^0 ($\propto K_3^0$, value characteristic of the nematic phase without smectic fluctuations) arbitrarily chosen at $T/T_{N1} = 0.99$. (The error bar, is an estimate of the inaccuracy resulting from this procedure.) The solid line is calculated from

$$\delta K_3 \propto \frac{1}{\sqrt{1 + \left(\dfrac{t - 0.878}{0.007}\right)^2}} .$$

sitions appear weakly first order and are not well described by a Landau type of mean field theory the critical exponents in both cases are identical (i.e. $\nu \simeq 0.67 \pm 0.05$); again indicating the similarity of the high and low temperature nematic.

In summary we have demonstrated that the principle experimentally observed properties of reentrant nematic phases can be understood simply in terms of an optimum density for smectic ordering. The Landau theory expresses this qualitative idea in quantitative forms through the demonstration that the ratio α_N/β_N required to fit the data is the value expected from independent measurements. Although Clark previously [14] argued that the phase boundary should be elliptical, rather than parabolic, in the *P-T* plane, the extra terms required to change the parabolic form into the elliptical are small in comparison with the quadratic term in eq. (2).

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